PATENT SPECIFICATION

DRAWINGS ATTACHED

1051521

1051521

Date of Application and filing Complete Specification: Jan. 27, 1965.

No. 3320/65.

Application made in Israel (No. 20834) on Feb. 20, 1964.

Complete Specification Published: Dec. 14, 1966.

Index at acceptance:—C1 A (11, D10, G13) AG13D10

Int. Cl.:—C 01 b 25/18

COMPLETE SPECIFICATION

Improvements in or relating to a process for the production of Substantially Iron Free Aqueous Solution of Phosphoric Acid

We, ISRAEL MINING INDUSTRIES — INSTITUTE FOR RESEARCH AND DEVELOPMENT, an Israeli Corporate Body of Haifa Bay, Near Irganim, Israel, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention generally relates to a method of removing iron from aqueous solutions containing phosphoric acid, hydrochloric acid, and chlorides of iron.

More particularly the invention relates to a method of removing iron from aqueous solutions resulting from the reaction of hydrochloric acid or a mixture of hydrochloric and sulfuric acid, on phosphate rock and containing phosphoric acid, hydrochloric acid, possibly some sulfuric acid, and chlorides and possibly sulfates or iron and of other cations present in phosphate rock.

Phosphate rock consists mainly of tricalcium phosphate along with impurities, which may include iron in amounts reaching as high as 10 to 15% by weight Fe_2O_3. For example, Moroccan and Kola phosphate rocks may contain from 0.1 to 0.7% by weight Fe_2O_3, Florida pebble from 1 to 2% by weight Fe_2O_3, Tennessee brown rock from 2.2 to 3.4% by weight Fe_2O_3, and mixed apatite-iron ores such as the Rocky Mountain and leached zone ores from 10 to 15% by weight Fe_2O_3.

The production of phosphoric acid from phosphate rock such as Moroccan, Kola and Florida pebble rock, by the process set out, for example, in British Patent 805,517, results in phosphoric acid which is of a quality and concentration much superior to that obtained by the conventional "wet process" (acidulation with sulphuric acid) from the same rocks. Even so, phosphoric acid produced by the aforesaid Patent No. 805,517 process does not —without further purification—meet the standards which exist for certain pharmaceutical and food uses, since it contains some of the iron content present in the phosphate rock, and for such specialized uses, even very small amounts of iron are undesirable.

While the problem of removing iron from the dissolution liquor resulting from acidulation of phosphate rock with hydrochloric or a mixture of hydrochloric and sulfuric acid exists where any type of rock phosphate is used as the raw material, it is particularly vexing when the rock phosphates have a high iron content. Not only is the presence of iron in the finally obtained phosphoric acid deleterious for the above-mentioned reasons, but additionally the presence of iron in the dissolution liquor represses the solubility of phosphoric acid in the solvent, and makes solvent extraction of the P_2O_5 content from such liquors e.g., in the manner described in Patent No. 805,517 more difficult as will be pointed out hereinafter.

Our procedure for iron removal is particularly applicable to, but by no means limited to, the production of iron-free or substantially iron-free phosphate rock dissolution liquors for further processing by the solvent extraction procedures for phosphoric acid recovery described in the aforesaid Patent No. 805,517. Our process is also applicable to the production iron-free phosphate rock dissolution liquors obtained by other methods, for example, the decomposition of rock phosphate with a mixture of hydrochloric and sulfuric acid, as already mentioned, or by absorption of HCl from by-product gas mixtures dilute in HCl in a phosphate rock slurry. In the latter process the decomposition of phosphate rock and absorption of HCl are effected concurrently resulting directly in the production of a phosphate rock dissolution liquor.

Following the procedure set out in, for example, the British patent No. 805,517, acidulation of phosphate rock with aqueous hydrochloric acid results in a dissolution liquor

[Price

BEST AVAILABLE COPY

containing phosphoric acid, hydrochloric acid and the chlorides of the cations, e.g., calcium, iron, and magnesium, present in the rock. By the use of suitable solvents, for example, aliphatic alcohols having from 4 to 12 carbon atoms, ketones and certain groups of amides, some of which are described in the patent, the phosphoric acid is recovered from such dissolution liquor.

To obtain a favourable distribution coefficient of P_2O_5 toward the solvent used to extract it, the decomposition of the phosphate rock should be effected with an excess of hydrochloric acid over the equivalent of the phosphoric acid content of the phosphate. But on the other hand, use of excess hydrochloric acid results in the undesirable coextraction of that free hydrochloric acid by the organic solvent used for extracting the phosphoric acid; for the latter reason it is advantageous to have as little excess hydrochloric acid present as possible, so as not to unduly burden the ensuing concentration and recovery operations which are included in the process of British Patent No. 805,517.

While the foregoing process has been shown to be very successful commercially for producing high quality phosphoric acid, yet as mentioned above, even in such a selective procedure some iron is extracted by the solvent, along with the phosphoric acid, and remains in the recovered product as a contaminant.

It is therefore an object of the present invention to provide a procedure for removing iron from aqueous solutions containing phosphoric acid, hydrochloric acid, possibly sulfuric acid, chlorides and possibly sulfates of cations, including iron, present in phosphate rock.

An additional object of this invention is to provide a method of removing iron from dissolution liquor resulting from the reaction of hydrocarbon acid or a mixture of hydrocloric and sulfuric acid, on phosphate rock or mixing wet-process phosphoric acid with a calcium chloride solution.

It is an additional object of the invention to effect the removal of iron from an aqueous solution containing phosphoric acid, hydrochloric acid, possibly sulfuric acid, chlorides and possibly sulfates of cations present in phosphate rock, without adding further contaminants to the solution.

A still further object of the invention is to provide a procedure which results in the production of an aqueous solution containing phosphoric acid, hydrochloric acid, possibly sulfuric acid, chlorides and possibly sulfates of cations present in phosphate rock, said solution being substantially free of iron, and adaptable for the ready and efficient recovery of phosphoric acid therefrom by known solvent extraction procedures.

The invention consists in a method of producing a substantially iron-free aqueous acidic solution containing phosphate, chloride and possibly also sulphate anions and cations present in phosphate rock, which may be further processed to produce phosphoric acid, from an aqueous liquid containing the above-said ions and also iron, which comprises extracting said liquor with a solvent selected from the group consisting of aliphatic alcohols, ketones, and esters of limited mutual miscibility with water, the total volume of solvent used being less than the volume of said liquor, and separating the iron-containing extract from the liquor.

By means of a solvent of the kind defined above the iron ions which are in the tervalent state are extracted preferentially. At the same time a certain quantity of phosphoric acid will as a rule be co-extracted. Where it is desired to recover the co-extracted phosphoric acid use can be made of the fact that iron chloride and sulfate in the ferrous state are much more soluble in water than in the organic solvent. Therefore, in accordance with a particularly suitable method for the recovery of co-extracted prosphoric acid the organic solvent extract obtained in accordance with the invention is first submitted to a treatment by which all Fe^{+++} is reduced to Fe^{++}, which is then followed by the removal of the ferrous salts, either by water extraction or by allowing the salts to precipitate. The remaining organic phosphoric acid solution which is substantially iron-free, is then recycled.

The process according to the invention will be further apparent from the following detailed description, given in connection with the attached drawings which show a diagrammatic flow sheet of illustrative embodiments of the process wherein the broken lines indicate the flow of the solvent stream and the solid lines indicate the flow of the aqueous stream.

As shown in Figure 1, dissolution liquor resulting from the reaction of hydrochloric acid and phosphate rock, and containing phosphoric acid, chlorides of cations present in phosphate rock including iron, and preferably from 40 to 80 grams per liter of hydrochloric acid (i.e., from 1.1 to 1.6N) is delivered through lines E and F to a liquid-liquid extractor of conventional design, such as a multistage mixer-settler, shown at A, where it is contacted with a predetermined, limited amount of an organic solvent according to claim 1, introduced through line K, resulting in the extraction of iron, along with some phosphoric acid. The iron is, we believe, in the form of the complex $HFeCl_4$ and dissolves readily in the solvent even at the relatively low hydrochloric acid concentration of the dissolution liquor, and despite the solution impeding effect of the phosphoric acid. We believe that the ready solubility of the iron in the solvent is due at least partly to the chlorides present in the liquor, particularly the calcium chloride.

The resulting extract, on leaving the extrac-

tor A through line H contains, as above mentioned, the iron complex and some phosphoric acid, and may have an iron content of for example, about 20.0 grams per liter or more compared with an iron content of 2.5 grams per liter in the original dissolution liquor. This iron-rich extract proceeds through line H to a stripper B which may be a liquid-liquid extraction system of conventional design such as a multi-stage mixer-settler, in which phosphoric acid is stripped from the extract by contacting it with an aqueous reflux containing ferric chloride and hydrochloric acid and introduced through line L. The resulting aqueous recycle containing, for example, about 40 grams per liter of iron, and some P_2O_5, returns to the dissolution liquor stream through line M as shown at C. On leaving the stripper B, the extract containing iron and hydrochloric acid is passed through line J to a washing means D where it is subjected to a washing step by being counter-currently contacted with water introduced through line P in a conventional liquid-liquid extraction means, the iron removed therefrom by dissolution in the water, and the resulting aqueous ferric chloride concentrate delivered partly to the stripper at B and partly removed from the system through line N from which it is either discharged to waste or treated for recovery of its ferric chloride or other values.

From the washer D, the washed solvent is returned to the extractor A through the line K as shown, for the counter-current extraction of the iron content of the dissolution liquor. After the iron extraction step in extractor A, the purified dissolution liquor passing through line G, now essentially iron-free, is ready for use as the input dissolution liquor whose phosphoric acid content is to be recovered, preferably by a solvent extraction procedure such as shown an described in the aforesaid British Patent 805,517. There may be many variations of the process illustrated in the drawing. For example, the stripper B may be eliminated when the solvent that is employed is highly selective for iron or when the cost of constructing and operating the stripper is not justified by the amount of P_2O_5 recovered from the solvent stream.

It is to be noted that the volume of solvent used in the process according to the invention to effect the efficient extraction of iron, is substantially less than the volume of solvent used for phosphoric acid extraction in the process described in the aforesaid British Patent No. 805,517.

In our process the volume of solvent used for extraction of iron from the dissolution liquor is less than the volume of the liquor, and is preferably in the proportion of from 0.1 to 0.2 volumes of solvent per volume of dissolution liquor.

In general, although the process described includes a circulating inventory of iron in both the solvent and the aqueous streams, substantially all of the iron entering the system at E is removed from the system at N, and substantially all of the P_2O_5 entering the system at E is recovered in the aqueous stream at G.

As an illustrative specific example of a process in accordance with our invention and with the flow diagram just described, the composition of the streams at the various points of the process illustrated in the flow sheet, are as shown in the following Table A:

TABLE A

	Concentration g/l						
	E	F	G	H	J	K	N
P_2O_5	100	104	100	40.7	0	0	0
HCl	60	61.5	53	50	50	0	100
H_2O	825	830	830	90	88	68	—
$CaCl_2$	330	290	330	1.7	1.7	0	3.3
Fe	2.5	4.0	0.07	17.6	17.6	0	40
Iso-amyl alcohol	—	—	—	666	666	750	20

Among the solvents which may be used in our process of pre-extraction of iron are the aliphatic alcohols, preferably those with more than 5 carbon atoms, ketones, and esters, containing from 5 to 18 carbon atoms, lower aliphatic alcohols having from 4 to 12 carbon atoms and ketones of limited mutual miscibility with water; and mixtures of any of the foregoing with organic liquids, such as nitrobenzene, which have a dielectric constant from 27 to 45 and function as co-solvents.

Tables B, C, D, E, F and G below illustrate embodiments of our invention in which solvents other than the iso-amyl alcohol illustrated in Table A were used.

TABLE B

Amyl Acetate Solvent

	Concentration in grams per liter		
	E	H	G
P_2O_5	110	9.2	100
Fe	2.7	25.8	0.01

TABLE C

Di-iso butyl ketone

	Concentration in grams per liter		
	E	H	G
P_2O_5	100	2.8	101
Fe	3.1	17.4	0.005

TABLE D

Hexanol Solvent

	Concentration in grams per liter		
	E	H	G
P_2O_5	100	22.6	95.5
Fe	3.6	26.9	0.07

TABLE E

Octanol Solvent

	Concentration in grams per liter		
	E	H	G
P_2O_5	100	20	96
Fe	3.1	25.2	0.07

Regarding the use of the co-solvents, e.g., nitrobenzene shown in Table G above, we have found that nitrobenzene by itself has no extraction power towards phosphoric acid; we also have found, unexpectedly, that by mixing nitrobenzene with an aliphatic alcohol—for example, that it exerted an inhibitory effect on the solution of phosphoric acid. With such a co-solvent system using iso-amyl alcohol and nitrobenzene as the co-solvents it appears, then, that a double synergistic effect occurs in which the extractibility of iron is increased while that of the phosphoric acid is decreased. An example of this is set out in Table J below:

TABLE J

Limiting Concentrations for Mixtures of Iso-Amyl-Alcohol-Nitrobenzene and Dissolution Liquor

	Mixed Solvent Phase		
Molar Ratio Nitrobenzene to Iso-Amyl Alcohol	P_2O_5 g/l	Fe g/l	Remarks
0	40.7	17.6	Using iso-amyl alcohol with a dissolution containing 2.8 g/l Fe and 98 g/l P_2O_5
0.3	21.0	30.0	do.
0.6	12.4	29.2	do.
1	6.0	24.8	do.
3	2.5	16.9	do.

Consideration of the figures in Table J, illustrates the synergistic effect mentioned above. Thus, at a molar ratio of 0.3 nitrobenzene to amyl alcohol, the iron content in the solvent reached a maximum and the P_2O_5 decreased appreciably with increasing amounts of nitrobenzene.

Quite generally it may be advantageous to admix with the solvent an organic liquid having a dielectric constant between 27 and 45.

From Tables D and E above, it will be seen that at a given free hydrochloric acid level the extraction capacity for ferric iron of alcohols such as n-hexanol, and n-octanol is somewhat higher than that of iso-amyl alcohol (17.6 grams per liter) and that the P_2O_5 which is co-extracted is much less than is the case with iso-amyl alcohol (40.7 grams per liter).

From Table K below, it is seen that amyl acetate is even more efficient than hexanol and octanol due to its high extraction power towards ferric chloride and its correspondingly low extraction power towards phosphoric acid.

TABLE K

Multistage Countercurrent Extraction of Dissolution Mixture with Amyl Acetate, in grams/liter

Stream		H+	P_2O_5	Fe	Cl	HCl
E	Dissolution Liquor Feed	3.0	110	2.7	244	53
G	Aqueous phase after extraction		100	0.010	224	
H	Solvent phase after extraction		9.2	25.8	67.5	

From the table above it is seen that amyl acetate show a relatively low extraction power for P_2O_5 (9.2 grams per liter) and a fairly high one for iron. Using this solvent, the iron in the dissolution liquor was reduced from 2.7 grams per liter to 10 parts per million. The amount of P_2O_5 which was co-extracted with the ferric iron would constitute a loss of

only 0.85% by weight on initial P_2O_5 if no further recovery step is made.

Figure 2 is a diagrammatic flow sheet of another embodiment of this invention in which the stripping and washing operations are replaced by a treatment by which all the Fe^{+++} is reduced to Fe^{++}. Basically this embodiment of the process is similar to the one described hereinbefore with reference to Fig. 1 and comprises feeding the dissolution liquor resulting from the reaction of hydrochloric acid and phosphate rock through line E_1 to a liquid-liquid extractor A_1, where it is contacted with a predetermined, limited amount of an organic solvent according to claim 1 introduced through line K_1 and withdrawing a substantially iron-free aqueous liquor at G_1. The extract leaving extractor A through line H_1 is fed into a unit Q which may, for example, be a multistage mixer settler and wherein it is contracted with iron powder for the reduction of any Fe^{+++} to Fe^{++}. For the withdrawal of the Fe^{++} it is possible either to induce phase separation inside unit Q by the addition of water through line P_1 or, alternatively, to bring about precipitation of a ferrous salt. In either case the iron is withdrawn from unit Q through line N_1 in form of an aqueous Fe^{++} solution or in form of a precipitated salt, as the case may be. The organic solvent and any co-extracted P_2O_5 is returned from unit Q through line K_1 to extractor A_1.

The compositions of the various streams in grams per litre are given in the following Tables L and M of which the former refers to the case where phase separation is induced inside the unit Q by the addition of a small amount of water, and the latter refers to the case where a ferrous salt is precipitated. The small amount of water necessary to bring about phase separation cannot be determined precisely since it will depend on the system, and may vary from case to case.

TABLE L

Phase separation in unit Q by the addition of a small amount of water.

	E_1	H_1	N_1	K_1	G_1
P_2O_5	102	40	0	31.2	102
$CaCl_2$	330	1.7	5.8	0	330
Fe	2.5	21	200	1.3	0.07

TABLE M

Removal of iron in unit Q by precipitation

	E	H_1	N_1	K_1	G_1
P_2O_5	102	40	1.5	30.6	101
$CaCl_2$	330	1.7	3.0	0	330
Fe	2.5	21	$FeCl_2$ solid	1.5	0.07

From the forgoing detailed description of our invention it is clear that there is provided here an improved process for producing from aqueous solutions containing phosphoric acid, hydrochloric acid and chlorides of cations, especially iron, such as are found in phosphate rock, a substantially iron-free liquor, from which iron-free phosphoric acid of high purity and concentration can be readily extracted by known solvent extraction techniques.

Ferrous chloride is less soluble in the organic solvent than ferric chloride. Therefore, in the results as illustrated by Table L where water is added, ferrous chloride, being water soluble, does not precipitate. However, in the the results as illustrated by Table M, no water is added and therefore the reduction of ferric chloride to ferrous chloride is accompanied by precipitation of the latter.

WHAT WE CLAIM IS:—

1. A method of producing a substantially iron-free aqueous acidic solution containing phosphate, chloride and possibly also sulphate anions and cations present in phosphate rock, which may be further processed to produce phosphoric acid, from an aqueous liquor containing the above-said ions and also iron, which comprises extracting said liquor with a solvent selected from the group consisting of aliphatic alcohols, ketones, and esters of limited mutual miscibility with water, the total volume of solvent used being less than the volume of said liquor, and separating the iron-containing extract from the liquor.

2. Method according to claim 1, wherein the volume of solvent used is in the proportion of from one volume of solvent to 5 to 10 volumes of said liquor.

3. Method according to claim 1 or 2, wherein the solvent is an aliphatic alcohol containing more than 5 carbon atoms.

4. Method according to claim 1 or 2, wherein the solvent is iso-amyl alcohol.

5. Method according to claim 1 or 2, wherein the solvent is amyl acetate.

6. Method according to any one of the preceding claims, wherein said liquor contains from 40 to 80 grams per liter of hydrochloric acid.

7. Method according to any one of the preceding claims, wherein the said solvent is admixed with an organic liquid having a dielectric constant from 27 to 45.

8. Method according to claim 7, wherein the said organic liquid is nitrobenzene.

9. Method according to any of the preceding claims wherein said extract which also contains co-extracted phosphoric acid is submitted to a treatment by which the iron ions are reduced from the tervalent to the bivalent state, the salts of bivalent iron are removed from the extract and the remaining organic-solvent solution of phosphoric acid is recycled.

10. Method according to Claim 9, wherein the bivalent iron salts are separated by precipitation.

11. Method according to Claim 9, wherein the bivalent iron salts are separated by extraction with water.

MARKS & CLERK,
Chartered Patent Agents
Agents for the Applicant(s).

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press (Leamington) Ltd.—1966. Published by the Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.

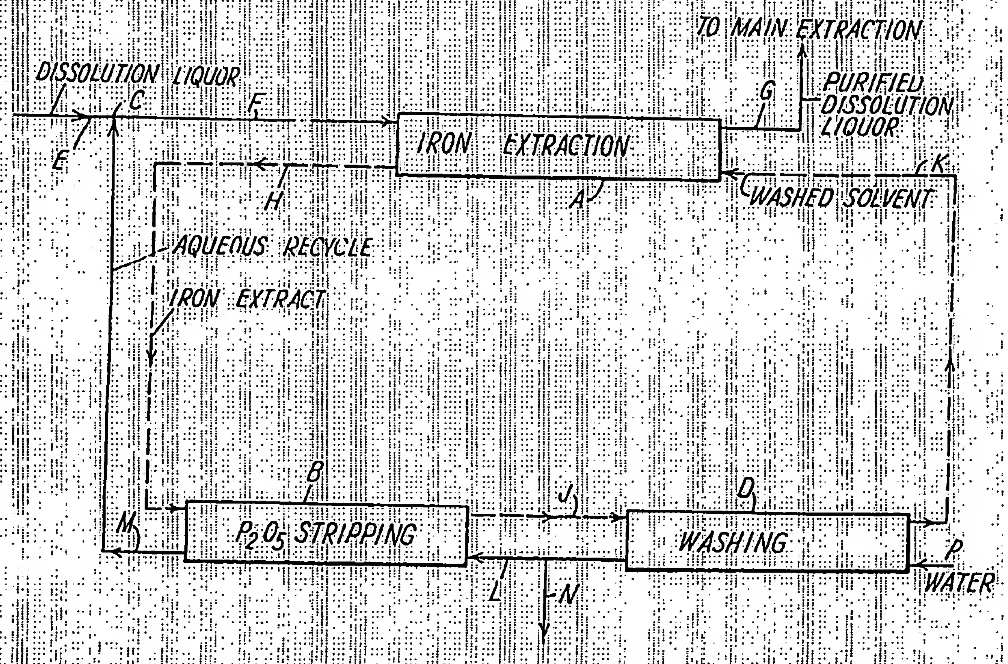
TO MAIN EXTRACTION
DISSOLUTION LIQUOR
C
F
G
PURIFIED DISSOLUTION LIQUOR
E
IRON EXTRACTION
H
A
K
WASHED SOLVENT
AQUEOUS RECYCLE
IRON EXTRACT
B
J
D
M
P_2O_5 STRIPPING
WASHING
P
WATER
L
N

FIG.I.

1051521 COMPLETE SPECIFICATION
2 SHEETS This drawing is a reproduction of the Original on a reduced scale
Sheets 1 & 2

FIG.1.

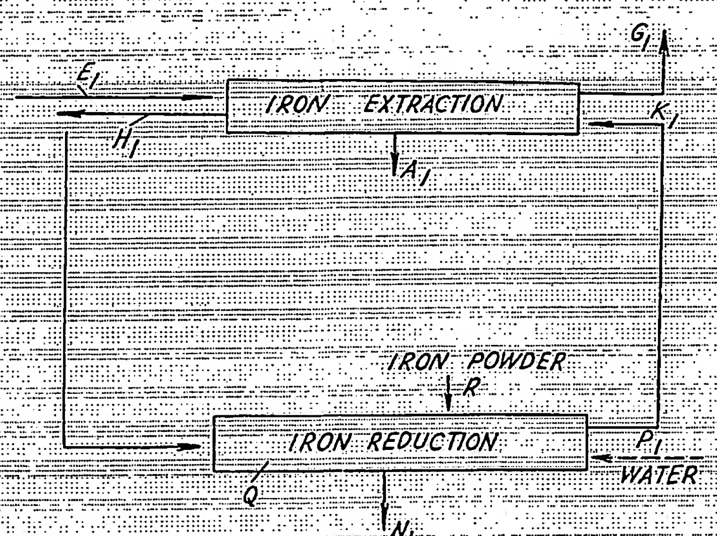

FIG.2.

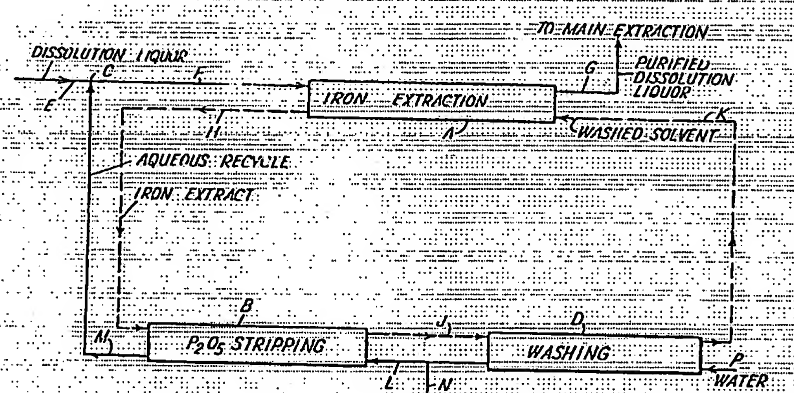

FIG.1.

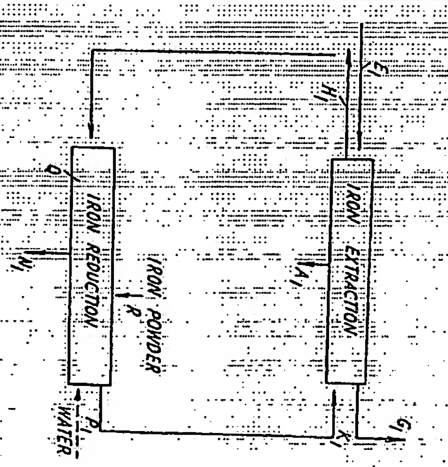

FIG.2.

1051521 COMPLETE SPECIFICATION
2 SHEETS This drawing is a reproduction of the Original on a reduced scale
Sheets 1 & 2